

Hydrogenation of Crude Oil at Elevated Pressure

Application Note

Energy

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Pyrolysis-GC/MS is a simple tool for the characterization of various crude oils. Rapid heating of approximately 0.5 - 1 μL of the oil volatilizes it directly to the GC where it is then analyzed like any other complex mixture. The bottom chromatogram in Figure 1 shows just Py-GC/MS in helium of such a crude oil. The addition a catalytic reactor, a pressure regulator and a trap to the system permits treating the oil in a reactive atmosphere, such as hydrogen, at higher pressures. The sample is volatilized by the Pyroprobe, and the resulting compounds are then carried in the reactant gas through the reactor to the trap, which is positioned after the back-pressure regulator. The hydrogenated products are collected by the trap, which is then thermally desorbed to the gas chromatograph. The middle chromatogram in Figure 1 shows the effect of heating the oil at 600°C in hydrogen at 100 PSI, with the flow going through a reactor with a platinum catalyst at 500°C. Under these conditions, compounds with double bonds are hydrogenated, converting olefins to paraffins. This effect is seen more easily in Figure 2. Here a series of olefins is marked with "O"s in the standard Py-GC/MS run on the bottom. Using a hydrogen carrier at 100 PSI, these olefins are completely hydrogenated, so the peaks are absent in the upper chromatogram.

If the pressure is increased further, the effect is to generate aromatics. For the upper chromatogram in Figure 1, the reactor temperature is still 500°C, but the pressure is now 400 PSI. Benzene, toluene, xylenes and heavier aromatics are generated in large quantities, although some of the aliphatics may still be seen. In addition, the chromatogram is now characterized by an increase in early eluters and a considerable reduction in the less volatile compounds from the original crude oil.

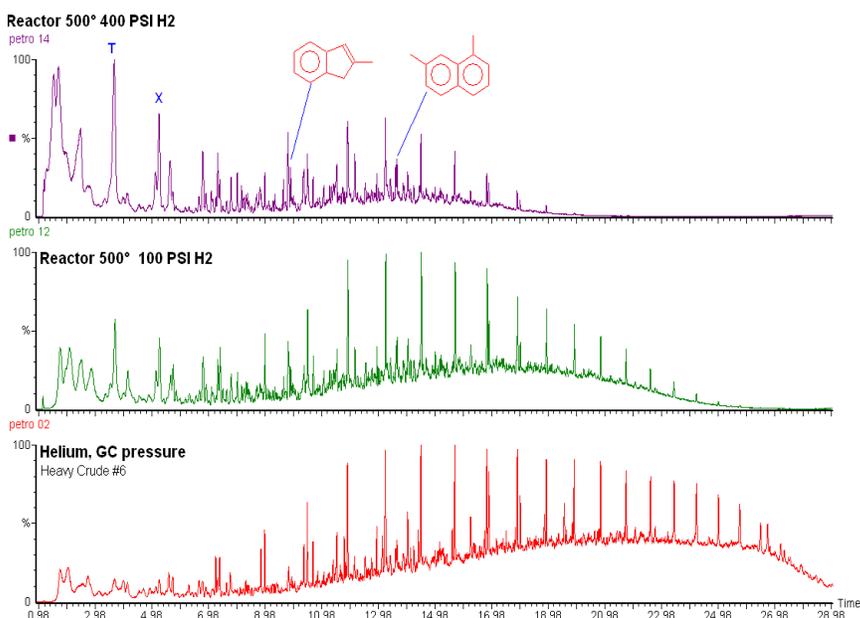


Figure 1: Py-GC of crude oil, bottom, at 100 PSI Hydrogen, center and at 400 PSI, top.

CDS HP-R Pyroprobe Conditions:

Interface: 325°C for 4 minutes
Pyrolysis: 600°C for 15 seconds
Reactor: 500°C, Platinum
Pressure: 100 PSI, 400 PSI
Trap: 325°C for 4 minutes

GC Conditions:

Column: 30m x 0.25 mm 5% phenyl
Carrier: Helium, 50:1 split
Program: 40°C for 2 minutes,
10°/min to 300°C
Detector: MSD
Mass range: 35 to 600 amu

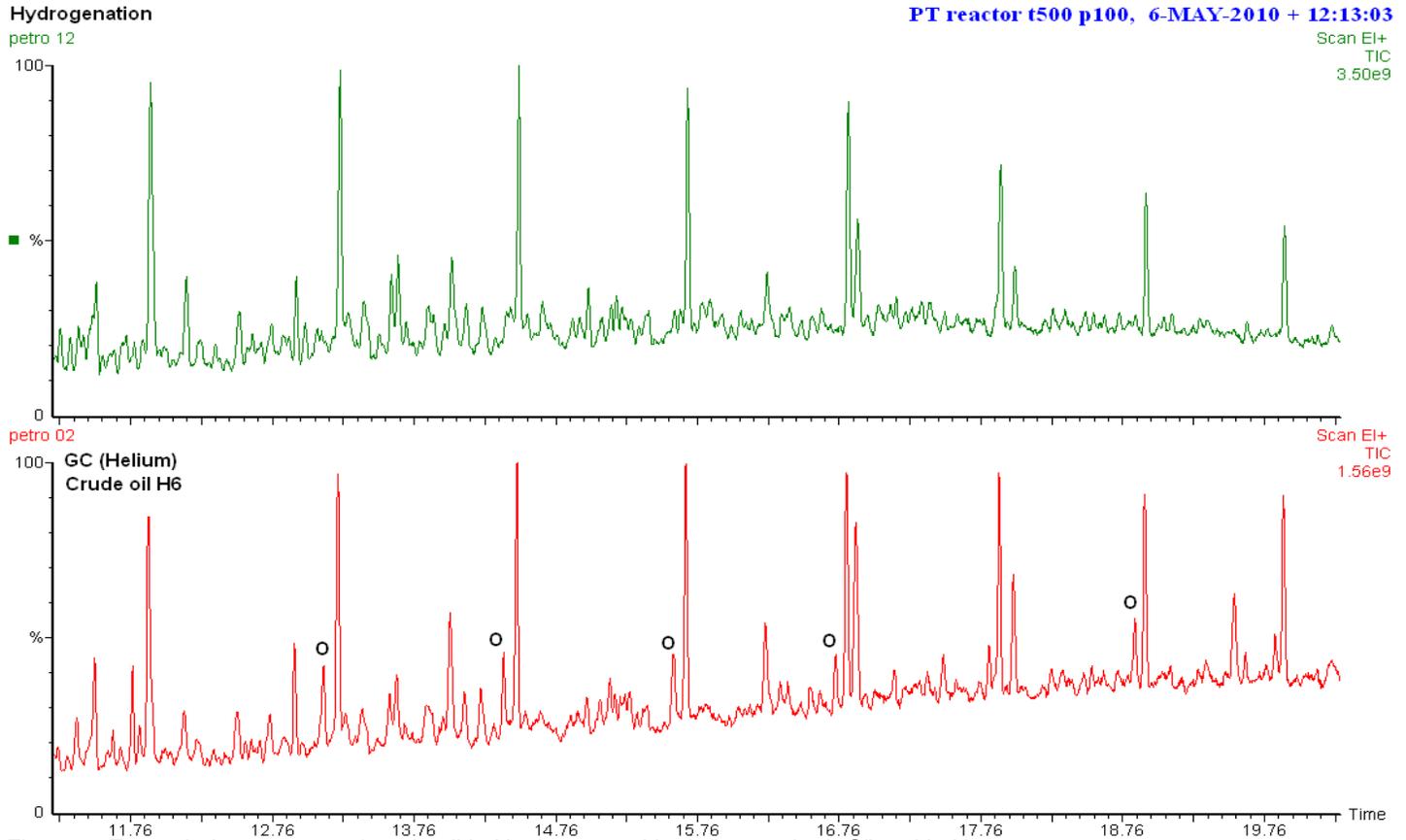


Figure 2: Expanded pyrograms of crude oil in He, bottom, with olefins marked "O" and in H2, top.